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PITTSBURGH UNIV PA DEPT OF CHEMISTRY
INTERMETALLIC COMPOUNDS CONTAINING LANTHANIDES (STUDIES OF MAGN--ETC(U)
MAY 77 W E WALLACE

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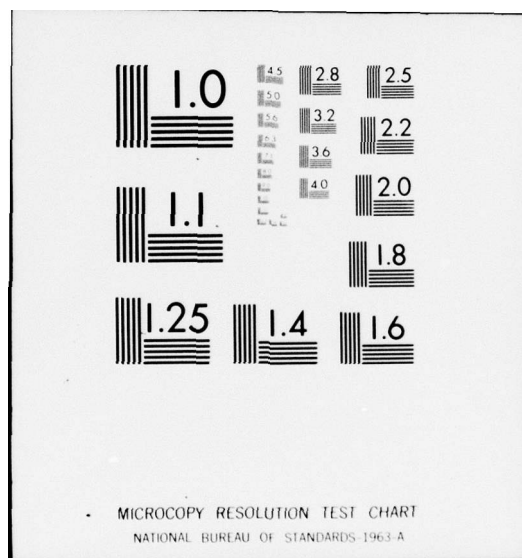
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INTERMETALLIC COMPOUNDS CONTAINING LANTHANIDES

(STUDIES OF MAGNETIC ANISOTROPY)

by

W. E. Wallace

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The findings in this report are not to be construed as an official Department of Army position, unless so designated by other authorized documents.

I. INTRODUCTION

Intermetallic compounds are formed by the lanthanide elements with many of the other metals in the periodic table. These materials have been under investigation in this laboratory for about two decades. Studies carried out in this laboratory and elsewhere has revealed many interesting effects - very powerful magnetocrystalline anisotropies, giant magnetostriction effects and extensive solvent power for hydrogen. The powerful magnetic anisotropy of these materials makes them of practical importance in the fabrication of high energy permanent magnets. These can in turn be used in a variety of devices - traveling wave tubes, electric motors, watt-hour meters, frictionless bearings, guidance systems, etc. The essential features of these substances which make them of utility as high energy magnetic materials have been described in two relatively recent monographs.^{1,2} Basically, the powerful magnetism is due to the crystal anisotropy. The quantum mechanical details of the lanthanide contribution to this have been worked out and published³ during the present contract period. The author regards this as a major contribution.*

Two themes have characterized the work of the preceding three-year period: (1) studies designed to trace the powerful permanent magnetism of rare earth-transition metal systems back to First Principles and (2) investigations directed toward improving our understanding of the magnetic interactions in rare earth-transition metal systems. The purpose of the latter is to set the stage for controlling magnetic structure and thereby being able to produce magnetic structures as desired by appropriate alloying.

The rare earth contribution to the magnetic anisotropy has been established to be a crystal field effect. This elucidation has come about after rather detailed studies of the crystal field interaction. This has involved

* Assistant Professor V. U. S. Rao and Research Assistant Professor S. G. Sankar were significantly involved in this investigation.

three kinds of experiment - magnetization measurements, specific heat determinations and the study of spin-disorder resistivity. These experiments have been examined using the quantum mechanical formalism known as the equivalent operator method. The crystal field studies are summarized in section II.

The magnetic anisotropy originates only in part with the rare earth sublattice; the transition metal sublattice also contributes, but in most cases to a minor extent.

A number of experiments have been carried out to elucidate the contribution of the transition metal sublattice. These are summarized in section III.

Several investigations have been carried out to reveal various other characteristics of the magnetic interactions in rare earth-d transition metal intermetallics. These are summarized in section IV.

It should be clear that the three-year program being summarized in this report is only a segment of an on-going program which was initiated in early January, 1965 and is being continued at least until late February, 1979.

It should be equally clear that this report can and should give only an overview of the activity in the program. For the full story the reader should consult the papers listed below in sections II, III and IV.

II. STUDIES OF THE CRYSTAL FIELD INTERACTION

The aspect of the work of the past three years is described very well in two rather major review papers and in six research papers. These are as follows:

Review Papers

1. W. E. Wallace, "The Crystal Field Interaction in Relation to the Magnetic, Thermal and Transport Properties of Rare Earth Intermetallics and Hydrides," Proc. of the Conf. on Crystal Field Effects in Metals and Alloys, Montreal, Canada, June 26-29, 1974.
2. W. E. Wallace, S. G. Sankar and V. U. S. Rao, "Crystal Field Effects in Rare Earth Intermetallic Compounds," to appear in Structure and Bonding, Springer-Verlag.

Research Papers

1. J. V. Mahoney, W. E. Wallace and R. S. Craig, "Influence of the Crystalline Electric Field on the Heat Capacity and Resistivity of PrAl_3 ," J. Appl. Phys. 45, 2733 (1974).
2. S. G. Sankar, V. U. S. Rao, E. Segal, W. E. Wallace, W. Frederick and H. Garrett, "Magnetocrystalline Anisotropy of SmCo_5 and Its Interpretation on a Crystal Field Model," Phys. Rev. B11, 435 (1975).
3. J. V. Mahoney, W. E. Wallace, R. S. Craig and S. G. Sankar, "Study of the Crystal Field Interaction in NdAl_2 by Measurements of Heat Capacity, Susceptibility and Resistivity," Inorg. Chem. 14, 2918 (1975).
4. T. Inoue, S. G. Sankar, R. S. Craig, W. E. Wallace and K. A. Gschneidner, Jr., "Low Temperature Heat Capacities and Thermal Properties of DyAl_2 , ErAl_2 and LuAl_2 ," J. Phys. and Chem. of Solids 38, 487 (1977).
5. S. G. Sankar, S. K. Malik, V. U. S. Rao and W. E. Wallace, "Effect of Magnetic Anisotropy on the Heat Capacity of HoAl_2 ," Crystal Field Effects in Metals and Alloys, A. Furrer, ed., Plenum Press, New York (1977), p. 153.
6. T. Inoue, S. G. Sankar, R. S. Craig and W. E. Wallace, "Influence of the Crystal Field Interaction on the Thermal Behavior of ErAl_2 , *ibid.*, p. 143.

The first of the review papers consists of 31 pages, the second of 98 pages. There is no way to summarize these lengthy papers except to say that, as noted in the Introduction, three methods have been developed to enable the crystal field interaction to be established. Additionally, it is to be noted that the strength of this interaction is kT with T of the order of two or three hundreds of degrees kelvin. Thus it is comparable with exchange, actually usually larger. The present report can serve the purpose of informing the reader of the existence of the two reviews. The first is not widely available. The second, which includes the first, will be widely available upon publication.

Research papers 1 and 3 above are very similar. The first deals with PrAl_3 , the other with isostructural NdAl_3 . Because of the general similarity comments will be confined to the PrAl_3 study. Measurement of magnetic

susceptibility (χ), heat capacity (C_p) and electrical resistivity (ρ) were made. There were clear indications of the effect of the crystal field interaction on χ , C_p and ρ . Analysis of this showed the spectrum for Pr^{3+} given in Table I.

Table I
Energy Levels and Eigenfunctions for Pr^{3+} in PrAl_3

	Eigenfunctions	Moment	Energy	Coefficients
Γ_3	$a -3\rangle + a 3\rangle$	0.00 0.737	131.6	
Γ_5	$b +4\rangle + c \mp 2\rangle$	-0.737 -0.426	126.5	
Γ_5	$c \mp 4\rangle - b \pm 2\rangle$	0.426	93.0	$a = 0.707$
Γ_4	$-a -3\rangle + a 3\rangle$	0.00 -0.250	87.9	$b = 0.6184$
Γ_4	$ \mp 1\rangle$	0.250	43.1	$c = 0.7858$
Γ_1	$ 0\rangle$	0.00	0.0	

It is to be noted that the ground state is a singlet and the overall splitting is 131.6°K. Results for NdAl_3 are generally similar, as might be expected in view of the structural similarity of these two compounds. Estimates of the overall splitting for Nd^{3+} in NdAl_3 range from 126 to 167°K.

Research papers 4, 5 and 6 deal with rare earth-aluminum Laves phase compounds. The overall splitting is about 100°K for RAl_2 phases with $\text{R} = \text{Dy}, \text{Er}$ and Ho .

Research paper 2 above provides a theoretical explanation for the strong magnetic anisotropy of SmCo_5 . Early work by Greedan and Rao⁴ provided an account of the anisotropy in RCo_5 and R_2Co_{17} phases using the operator equivalent

method. This formalism is satisfactory only when there is no mixing of J states, the situation for most of the rare earth intermetallics for which the multiplets are widely spaced. It is not so for Sm^{3+} , which is an especially interesting case because of the importance of SmCo_5 in permanent magnet fabrication. In this case the Racah algebra must be used. The Sm^{3+} sublattice anisotropy is properly accounted for using reasonable values of the crystal field intensity parameters ($A_2^0 \langle r^2 \rangle = -420^\circ\text{K}$, $A_4^0 \langle r^4 \rangle = -25^\circ\text{K}$, $A_6^0 \langle r^6 \rangle = 1^\circ\text{K}$ and $A_6^6 \langle r^6 \rangle = 6^\circ\text{K}$) and the Hamiltonian as follows:

$$H = \lambda \vec{L} \cdot \vec{S} + K_{\text{CF}} + 2\mu_B S H_{\text{ex}} \quad (\text{where } S = S_z \text{ or } S_x)$$

K_{CF} is evaluated by the tensor-operator technique devised by Racah.

$H_{\text{ex}}\mu_B/k = 240^\circ\text{K}$, where k is the Boltzmann constant.

The energy of the Sm^{3+} sublattice was calculated with moments parallel (z direction) and perpendicular (x direction) to the c-axis. The energy was found to be lower for the z direction by an amount that agreed well with results obtained experimentally by Frederick and Garrett of the Wright-Patterson Air Force Base. Thus the source of the powerful anisotropy and high energy of SmCo_5 permanent magnets has been established. Similar calculations were made by Buschow, Van Diepen and de Wijn⁵ at a slightly later time.

III. STUDIES TO ELUCIDATE THE TRANSITION ELEMENT SUB-LATTICE ANISOTROPY

During the preceding 3-year period 4 papers, all original research, were published in this area. They are as follows:

7. K. S. V. L. Narasimhan and W. E. Wallace, "Magnetic Properties of $\text{R}_2\text{Fe}_{17-x}\text{M}_x$ (R = Y, Ho and M = Ni, Al) and $\text{Y}_2-x\text{Th}_x\text{Fe}_{17}$ Compounds," AIP Conf. Proc., No. 18, 1248 (1974).
8. K. S. V. L. Narasimhan, W. E. Wallace, R. D. Hutchens and J. E. Greedan, "Magnetic Anisotropy of R_2Co_{17} Compounds (R = Er, Tm, Yb)," *ibid.*, No. 18, 1212 (1974).

9. K. S. V. L. Narasimhan, "Magnetic Anisotropy of Fe, Mn and Ni Substituted ErCo_{17} Ternaries," IEEE Trans. Mag, MAG 12, 1009 (1976).
10. K. S. V. L. Narasimhan, C. Do-Dinh, W. E. Wallace and R. D. Hutchens, "Magnetic Properties of the $\text{ThCo}_{5-x}\text{Ni}_x$ System," J. Appl. Phys. 46, 4961 (1975).

In RCo_5 intermetallics there are two crystallographically distinguishable varieties of cobalt - the so-called 2c and 3g cobalts. One wishes to know how each of these contributes to the magnetic anisotropy. In the R_2Co_{17} (or R_2Fe_{17}) intermetallics there are four kinds of Co (or Fe). Presumably each is contributing to the anisotropy each in its own special way. Additionally, in the R_2Co_{17} intermetallics there are two kinds of rare earths. Thus in the RCo_5 intermetallics there are three magnetic species and in the R_2Co_{17} intermetallics there are six. The role of the rare earths has been established theoretically but as yet this is an intractable approach for the d transition element sub-lattice. An experimental approach is accordingly necessary.

The strategy being followed is to substitute preferentially on the several sub-lattices and to study systematically the alteration in magnetic properties. Crystal chemical principles are used to arrange the preferential substitution. The first example of this was⁶ the study of $\text{R}_2\text{Co}_{17-x}\text{T}_x$ with T = Fe or Mn. In these cases the sign of the anisotropy was changed by alloying with Fe or Mn.

Paper No. 7 involves R_2Fe_{17} -based ternaries with R = Y, Tm or Ho. Fe is partially replaced by Ni or Al. Fe is strongly magnetic in these materials ($\sim 2\mu_B$ per atom) whereas Ni is weakly magnetic ($\sim 0.3\mu_B$ per atom) and Al is non-magnetic. Yet when Fe is replaced by Ni or Al, T_c sharply increases. $\text{Tm}_2\text{Fe}_{17}$ was found to be an extremely interesting compound. Its magnetic structures are given in Table II.

Table IIMagnetic Characteristics of $\text{Tm}_2\text{Fe}_{17}$

T(°K)	Easy Axis	Structure
0-85	parallel to c-axis	Ferrimagnetic*
85-265	in basal plane	Ferrimagnetic*
265-285		Spiral
> 285		Paramagnetic

* The Tm and Fe moments are coupled anti-parallel.

The Fe sub-lattice has a preference for an easy axis in the plane, the Tm sub-lattice prefers c-axis uniaxiality. The latter predominates only at low temperatures. Replacement of Fe with Ni or Al decreases the Fe sub-lattice anisotropy in $\text{Tm}_2\text{Fe}_{17}$ and the 85°K transition (indicated in Table II) moves progressively upward, reaching 240°K in $\text{Tm}_2\text{Fe}_{14}\text{Al}_3$. The suggestion is that Al has progressively replaced Fe in the 4f (i.e., dumbbell) crystallographic sites. These sites are recognized as the source of the strong basal plane anisotropy in R_2Fe_{17} or R_2Co_{17} phases.

Paper 8 deals with the determination of the easy axis in R_2Co_{17} with R = Er, Tm and Yb. The first two are uniaxial materials at 300°K, the latter appears to have a conical structure. Anisotropy fields (H_A) were determined and are given in Table III.

Table IIIAnisotropy Fields* for R_2Co_{17} Compounds

	$\text{Er}_2\text{Co}_{17}$	$\text{Tm}_2\text{Co}_{17}$	$\text{Yb}_2\text{Co}_{17}$
4°K	30	70	30
300°K	18	18	19

* in kOe

Paper 9 represents a continuation of the work in paper 8, focusing attention on $\text{Er}_2\text{Co}_{17}$. As noted above, it is uniaxial but has a fairly low value of H_A . The work of Schaller et al.⁶ showed the uniaxiality could be induced in basal plane R_2Co_{17} systems by partially replacing Co with Fe or Mn. This suggested that H_A for $\text{Er}_2\text{Co}_{17}$ might be strengthened by partially replacing Co in it with Fe or Mn. The effect of Mn, shown in Table IV, is particularly dramatic.

Table IV
Anisotropy Fields and Curie Temperatures of
 $\text{Er}_2\text{Co}_{17-x}\text{Mn}_x$ Ternaries

x	$T_c(^{\circ}\text{K})$	$H_A(\text{kOe})$ at 4.2°K
0	1160	31
2	982	133
4	746	103
6	383	---

Work by Rothwarf, Leupold, Greedan, Wallace and Das on $\text{Th}(\text{Co}_{1-x}\text{Fe}_x)_5$ and $\text{Y}(\text{Co}_{1-x}\text{Fe}_x)_5$ ternaries suggested that the Co sub-lattice anisotropy originated primarily with the 2c Co atoms, i.e., those in planes with Th, Th being their nearest neighbors. Paper 10 deals with similar subject matter - the study of $\text{ThCo}_{5-x}\text{Ni}_x$ ternaries. Neutron diffraction work by Atoji, Do-Dinh and Wallace on these ternaries showed⁸ that Ni replaces Co preferentially at the 2c sites. Studies of the anisotropy fields of $\text{ThCo}_{5-x}\text{Ni}_x$ ternaries is consistent with this and also with the notion that the transition metal sub-lattice originates primarily with Co at the 2c positions.

Conclusions derived from the ARO-supported work at Pittsburgh are supported by recent polarized neutron diffraction studies by Deportes et al.⁹

We now have a reasonable idea as to anisotropy in the R_2Co_{17} and RCO_5 compounds and how to bring about "favorable" anisotropy, but do not know the

"why." Very sophisticated theory will necessarily be entailed in the full elucidation of these interesting phenomena

IV. MAGNETIC INTERACTIONS IN SELECTED INTERMETALLICS

In the grant period six research papers in this area have been published.

They are as follows:

11. L. T. Miskinis, K. S. V. L. Narasimhan, W. E. Wallace and R. S. Eraig, "Magnetic Properties of $Gd_{1-x}Th_xFe_2$ and $Gd_{1-x}Ce_xFe_2$," J. Sol. State Chem. 13, 311 (1975).
12. K. S. V. L. Narasimhan, V. U. S. Rao, W. E. Wallace and I. Pop, "Magnetic Properties of RMn_2X_2 Compounds (R = Rare Earth, Y or Th and X = Ge, Si)," AIP Conf. Proc. 29, 594 (1976).
13. M. Coldea, I. Pop, W. E. Wallace and K. S. V. L. Narasimhan, "Magnetic Characteristics and NMR of UCu_5 ," Magnetism Lett. 1, 11 (1976).
14. D. M. Gualtieri, K. S. V. L. Narasimhan and W. E. Wallace, "Magnetic Properties of the Hydrides of Selected Rare Earth Intermetallic Compounds with Transition Metals," AIP Conf. Proc. 34, 219.
15. M. Merches, K. S. V. L. Narasimhan, W. E. Wallace and A. Ilyushin, "Magnetic Properties of $R(Fe_{1-x}Mn_x)_2$ Compounds (R = Gd, Tb, Dy, Ho or Er)," AIP Conf. Proc. 34, 233 (1976).
16. K. S. V. L. Narasimhan, "Magnetic Characteristics of the $MnNiSi_{1-x}Ge_x$ Compounds Crystallizing in the Co_2P Type Structure," AIP Conf. Proc. 34, 40 (1976).

Papers 11, 12 and 14 all have the same ultimate objective: to attempt to manipulate the nature of rare earth-transition metal coupling by alloying in such a way as to change the electron concentration. An example of this is the study of the $Gd_{1-x}Th_xFe_2$ system in paper 11. When tetravalent Th replaces trivalent Gd it is expected that the electron concentration will be increased. Since the RKKY interaction, which presumably couples the Gd and Fe moments, is electron concentration sensitive, it was hoped that the ferrimagnetic Gd-Fe coupling in $GdFe_2$ could be made ferromagnetic in the ternaries. This did not develop. The Fe moment decreased, indicating that the extra electron provided by Th did not increase the electron concentration but instead was absorbed by Fe.

In paper 12 a series of compounds were studied, represented by the formula RMn_2X_2 where R = a rare earth, Y or Th and X = Si or Ge. These materials form in the $BaAl_4$ structure. A variety of magnetic behavior is observed for the 20 compounds studied. The original paper should be consulted for details. This work was to set the stage for work involving quaternary systems, e.g., $LaMn_{2-x}T_xGe_2$ where T = Cr, Fe, Co, Ni or Cu.

The effect of absorbed hydrogen on rare earth-Fe coupling was investigated in paper 14. The compounds RFe_2 with R = Ho, Er and Tm were investigated. These materials absorb hydrogen in copious amounts. The most significant results obtained are listed in Table V.

Table V

Magnetic Characteristics of Hydrogenated RFe_2 Systems

	Magnetization at 4.2°K μ_B per formula unit	Curie Temperature (°K)
$HoFe_2$	5.11	614
$HoFe_2H_{4.5}$	2.35*	287
$ErFe_2$	4.75	596
$ErFe_2H_{3.9}$	5.60**	280
$TmFe_2$	2.52	610
$TmFe_2H_{4.3}$	6.45**	270

* Measured at an applied field of 21 kOe.

** Measured at an applied field of 120 kOe.

Hydrogenation rather strikingly reduces the interactions, as reflected in the Curie temperature, and in the case of $ErFe_2$ and $TmFe_2$ increases the magnetization. The effect for $TmFe_2$ is striking. In RFe_2 the R and Fe moments are coupled antiparallel. The rise for $TmFe_2$ upon hydrogenation suggests that this may no longer be true for the hydrogenated material. The presence of hydrogen seems to have affected the Tm-Fe coupling. If the coupling has been reversed, it will be the first instance in which this has been accomplished.

Hydrogenated TmFe_2 and ErFe_2 are unusually difficult to saturate. Results are shown in the accompanying diagram. The source of this exceptional magnetic hardness is as yet unknown.

In paper 13 the bulk magnetic properties of (cubic) UCu_5 have been inter-related to its Cu NMR characteristics. U in this material behaves as a free tripositive ion as deduced from its susceptibility. Normally the light actinide metals exhibit only Pauli paramagnetism, indicating delocalized 5f electrons.¹⁰ In UCu_5 the U-U distance is $\sim 5\text{\AA}$ and the 5f electrons are localized. From the Knight shift dependence on temperature (or susceptibility) the strength of the s-f exchange has been established for the two non-equivalent copper sites. $J_{\text{sf}}(\text{I}) = -0.58 \text{ eV}$ and $J_{\text{sf}}(\text{II}) = -0.35 \text{ eV}$.

In paper 15 the magnetic properties of the ternaries $\text{R}(\text{Fe}_{1-x}\text{Mn}_x)_2$ ($\text{R} = \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}$) were studied. With three magnetic species present complex magnetic coupling schemes are possible. The study was carried out in an attempt to elucidate the coupling scheme. The transition metal sub-lattice moment is given in Table VI.

Table VI

Transition Metal Sub-lattice Moment (μ_B) in
 $\text{R}(\text{Fe}_{1-x}\text{Mn}_x)_2$ Systems

R	x				
	0	0.2	0.4	0.6	0.8
Gd	4.2	3.14	2.18	1.86	1.77
Tb	3.28	1.82	1.99	1.83	1.42
Dy	4.5	4.36	3.50	2.97	2.24
Ho	4.0	2.83	2.14	1.8	0.39*
Er	2.96	----	1.05	1.33	0.14*
Y	2.9	2.0	1.2	0.4	----

* C14 structures. All the other materials were in the cubic C15 structure.

The decline in transition metal moment could be due to simple dilution or antiferromagnetic coupling of Fe and Mn. Decision between these alternatives requires additional information, e.g., neutron diffraction studies. The best guess is that Mn carries a small moment ($< 0.5\mu_B$) aligned antiparallel to the Fe moment.

In paper 16 a study was made of the influence of substituting Ge for Si in MnNiSi. This compound is ferromagnetic with $T_c = 616^\circ\text{K}$ and a magnetic moment of $2.5\mu_B$. It was hoped that T_c and the magnetic moment could be enhanced by increasing the Mn-Mn distance, to be brought about by replacing Si with Ge. Single phase materials were produced for the range MnNiSi up to MnNiSi_{0.2}Ge_{0.8}. A rise of magnetization from 2.5 to $2.9\mu_B$ is found as Ge replaces Si but T_c declines steadily. The highest Ge content alloy is metamagnetic, but MnNiSi_{0.3}Ge_{0.7} and all lower content Ge alloys are found to be ferromagnetic.

The several studies involving Mn alloys represented attempts to form ferromagnetic systems in which Mn was contributing substantially to the magnetization. It is known that in the Hensler alloys Mn exhibits a moment of $5\mu_B$ per atom. In these materials the Mn-Mn distance is large ($> 3 \text{ \AA}$). It is also known that when the Mn-Mn distance is reduced below $\sim 2.8 \text{ \AA}$, the d electrons delocalize and the local moment vanishes. The several studies described were attempts to form compounds in which the Mn-Mn spacing was sufficiently large to bring out the large Mn moment - either this or to set the stage for other studies with this intent.

Many interesting features of Mn systems have been revealed - the effect on anisotropy, on T_c and on coupling. These effects warrant further attention.

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